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DEVELOPMENT OF THIN CONDUCTING FILM FABRICATION METHODS

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Oak Ridge, TN 37830

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Air Force Systems Command
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This technical report has been reviewed and is approved for publication.

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Fabrication of seamless cylindrical pyrolitic carbon foils with 5 cm radius, 2 cm height, and thickness as low as 10 $\mu g/cm^2$ was investigated. Chemical vapor deposition at 1050°C, flowing 1 part methane in 25 parts Argon at 4 ℓ/min through a 5 in diameter, 12 in tall graphite susceptor containing a stack of 5 cm radius, 2 in tall fused silica cylinders for 1 to 2 hours resulted in reproducible formation of pyrolitic carbon films weakly bonded to the inner surface of the fused silica cylinders. The carbon films ranged from < 20 to

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100 μg/cm², depending on deposition time. It proved possible to transfer the carbon foils intact from the formation mandrel (fused silica) to various intermediate mandrels (beeswax, polymeric resins such as PVA, PVC, PBS, Saran). Efforts to transfer the foils intact from formation on intermediate mandrels to electrode rings (to obtain free standing foils) were not successful for masses below 600 μg/cm². However, polymeric resin cylinders 600 μg/cm² were readily made.

CONTENTS

INTRODUCTION

Progress in the area of high energy plasma generation by electromagnetic implosion has received considerable attention in the past few years and is discussed in some detail by Turchi and Baker.[1] Scientists at the Air Force Weapons Laboratory in Albuquerque, New Mexico, have recently conducted similar experiments in which plasmas of $\sim$ 50 eV, 10^{12} W and 10^5 J have been produced using existing pulsed power facilities on free-standing arc section foils having masses of 100 to 300 μg/cm^2 and a diameter of 7 cm.[2,3] Theoretical calculations performed predict significant improvements in performance ($\sim$ 100 eV, 10^{13} W) by decreasing the mass, increasing the radius, and completely eliminating the seams. Thus, the need for development of methods for fabrication of thin (< 100 μg/cm^2), seamless cylindrical electrically conductive films has developed.

The primary objective of the study discussed in this report is to develop methods for fabricating a very thin (< 100 μg/cm^2) seamless cylindrical pyrolytic carbon film using chemical vapor deposition (CVD) technology and to investigate methods of film removal, shipping and attaching to test electrodes. The first part of this study has been further categorized according to CVD parameters and mandrel-substrate requirements.

CVD parameters investigated and found to affect film thickness, carbon structure, and mechanical properties include: deposition temperature and time, gas composition and ratios, and flow rates/velocity. The mandrel-substrate requirements of high melting point (> 1200°C), low coefficient of thermal expansion ($\sim 10^{-6}$ cm/cm°C), and nonporous/nonadhering surface resulted in the selection of fused silica for the mandrel-substrate material. Specific methods investigated for removing and transferring pyrolytic carbon films onto cylindrical electrodes consist of: (1) melted beeswax and other high molecular weight waxes, (2) polymeric resins (PVC, PVA, PBS, etc.), (3) naphthalene, and (4) aluminum disks.

Fabrication of thin pyrolytic carbon films by CVD techniques has been successfully demonstrated. Removal and tranfer of the pyrolytic carbon films from the mandrel to the electrodes has not yet been effected to the desired degree. Additional work in this area will be required for complete success of the endeavor.

THEORY

Chemical Vapor Deposition

Chemical vapor deposition involves the decomposition and condensation of vapor transported from the source feed onto a hot substrate. The hot substrate is partially responsible for thermally activating the reaction process.

Carbon was one of the first vapor-deposited materials prepared. It has been produced in larger quantities than any other deposited material, and the reactions involved have been studied for half a century. Despite this massive attention, the location and nature of the critical steps of the deposition reactions are still poorly defined. Many compounds have been used to deposit carbon, including the simple aliphatics and aromatics, carbon oxides, and halogenated and oxygenated hydrocarbons. However, methane is probably the most common source material for carbon deposition.

A recently published model for CVD of carbon[4] from which trends in the microstructure of the deposit can be inferred, consists of the following assumptions:

1. Gas-phase equilibrium exists at or near the deposition temperature.

2. Deposition results primarily from aromatic and acetylenic species.

3. The benzene (C_6H_6) and acetylene (C_2H_2) concentration can be used as measures of the concentrations of the relevant aromatic and acetylenic species, respectively.

4. Deposition from aromatic species at low deposition rates results in laminar deposits in which the graphite basal planes have a high degree of preferred orientation with respect to the substrate.

5. Deposition from aromatic species at high deposition rates results in sooting conditions and isotropic deposits.

6. Deposition from acetylenic species yields isotropic deposits.

For deposition at one atmosphere, the C_2H_2/C_6H_6 ratio varies from orders of magnitude below unity to orders of magnitude above it as the temperature is increased. Thus, at temperatures up to 1500 K (1225°C), benzene is the predominant carbon-bearing compound formed in the gas phase. This suggests that under nonsooting conditions, a laminar microstructure can be expected up to this temperature. However, other factors affecting conditions responsible for deposition of either laminar or isotropic microstructures include initial gas composition, gas ratios (dilution effects), and flow rates (velocity). In general, laminar deposits are expected at low deposition rates, while isotropic deposits are most usually obtained from either aromatic species at high deposition rates and from acetylenic species. Therefore, the microstructure of the deposit is dependent upon deposition temperature, gas composition/ratios, and flow rates.

EXPERIMENTAL

CVD-Substrate Mandrel

Chemical vapor deposition requires the use of a substrate which must be at an elevated temperature sufficiently high to thermally activate the reaction process. In this study methane gas was chosen as the parent hydrocarbon molecule which requires substrate temperature in excess of 900°C for deposition to occur. With this in mind, the following substrate requirements were imposed: (1) softening point > 1200°C, (2) CTE close to that of carbon (a-b plane $\sim 10^{-6}$ in/in/°C), and (3) nonadhering surface (extremely smooth and nonporous). After reviewing a list of potential candidates, the following three materials evolved as potential substrate materials: molybdenum, graphite, and fused silica. However, the first two materials were eliminated due to cost and high adherence (porous surface). Thus, fused silica, which was found to satisfy all of the imposed requirements as well as being readily available in a wide range of cylindrical sizes, was chosen as the substrate material for this study.

In this particular investigation, several 2.5-cm x 10-cm-diameter fused silica cylindrical mandrels were CVD coated simultaneously by placing them over a solid graphite cylinder enclosed in a graphite container such as shown in Figure 1. The carbon layer was deposited onto the inside of the quartz mandrel. Since the CTE of quartz is slightly lower than that of carbon, the carbon film will shrink away from the quartz mandrel upon cooling.

CVD Parameters

The CVD parameters investigated in this study include: initial gas composition, gas ratios, flow rates, and deposition temperature. In the initial part of this investigation, a highly ordered graphitic type of carbon deposit was desired due to higher modulus/stiffness which was thought to be necessary for self-supporting characteristics. Thus, the initial parameters were chosen to result in a laminar deposit. This was achieved by using a relatively high deposition temperature ($\sim$ 1250°C), and decreasing the deposition rate by using hydrogen in the initial gas composition. The exact parameters used in the initial runs together with other data are shown in Table 1. The initial concept of fabricating a high modulus self-supporting film by slowly forming a highly ordered laminar carbon deposit was abandoned when experimental results revealed the high modulus/brittle carbon film to be fracturing extensively upon cooling from the deposition temperature. This behavior was attributed to a combination of the anisotropic nature of the pyrolytic carbon and the thermal expansion mismatch between the quartz mandrel and the carbon film. At this time, it became evident that a more turbostratic type of carbon deposition having isotropic properties was needed. Thus, the deposition temperature was lowered to < 1100°C and the hydrogen gas was eliminated from the initial gas composition. These changes together with minor changes in gas flow rates resulted in a flexible weakly adhered film which was

Four 10-cm-diameter fused silica cylinders stacked on base of graphite vessel for CVD coating

Graphite containment vessel used in CVD coating

Figure 1. FUSED SILICA MANDRELS POSITIONED ON BASE OF GRAPHITE VESSEL FOR CVD OPERATION.

Table 1

EFFECTS OF CVD PARAMETERS ON PYROLYTIC CARBON FILM DEPOSITED

CVD Parameters				Film Properties				
Gas Composition	Ratios	Deposition Temperature (°C)	Deposition Time (hr)	Structure	Integrity	Flexibility	Adherence to Mandrel	Film Thickness ($\mu g/cm^2$)
H_2, CH_4, Ar	2:1:25	1250	4	Laminar	Good	Very Poor	Very High	400 - 800
"	1:1:25	1200	4	"	"	"	"	"
"	1:1:25	1100	4	"	"	"	"	"
"	0.5:1:25	1100	4	"	"	"	"	"
"	1:1:25	900	7	No deposit	-	-	-	-
CH_4, Ar	1:25	1150	4	Turbostratic	Good	Good	Low	200 - 400
"	1:25	1100	4	"	"	"	"	"
"	"	1075	4	"	"	Very good	Very low	100 - 200
"	"	1050	4	"	"	"	"	"
"	"	1000	4	No deposit	-	-		
"	1:25	1050	2	Turbostratic	Good	Very good	Very low	< 100
"	1:25	1050	1	"	"	"	"	< 20

capable of withstanding thermally induced stresses without fracturing. Once these parameters were established, the desired film thickness was obtained by controlling the deposition time. Scanning electron microscopy (SEM) micrographs of both types of deposits (laminar and turbostratic) are shown in Figures 2 and 3.

Film Removal

Fabrication of pyrolytic carbon films, by controlled CVD deposition of carbon onto the inside surface of a fused silica cylindrical mandrel, was found to be reproducible. However, removing and transferring of the film from the quartz mandrel onto cylindrical electrodes has not yet been entirely successful. Thus, increased effort in this area is indicated. Specific methods of removing and transferring films which have been investigated to date include: (1) melted wax, (2) polymeric coatings, (3) naphthalene, and (4) aluminum expansion disks.

Melted Wax. Several attempts at removing the carbon film from the quartz mandrel were made using melted beeswax, as in Figure 4. In the first few attempts, the entire coated cylinder was filled with melted wax. Upon cooling, the wax solidified, shrank, and caused the film, which adhered to the wax, to detach from the mandrel surface. This method initially appeared very promising. However, the excessive wax shrinkage could not be controlled effectively and excessive damage was imparted to the film.

Polymeric Resins. The use of thermoplastics in removing the carbon film from the quartz mandrel has been investigated and was found to be very promising. Specific plastics used in this study consisted of: polyvinyl alcohol (PVA), polyvinyl chloride (PVC), polyvinylidene chloride (Saran), and polybutylstyrene (PBS). These materials were used by preparing dilute solutions with an appropriate solvent (water for PVA). The carbon-coated mandrels were dipped into the polymeric solution being evaluated, removed, and allowed to dry by evaporation. The thickness of the polymeric film formed by this dipping process was controlled by the concentration of the solution prepared. Once the carbon-coated mandrel was covered with the polymeric film, the composite film (carbon film plus polymeric film) was removed from the mandrel by either cutting the edges and working a scalpel in behind the film or by first exposing the film to -40°C to shrink the polymeric film and accelerate the removal process as shown in Figure 5. Each polymeric system evaluated required different handling procedures and produced different results. This data, which is presented in Table 2, reveals that PVA and Saran are the most desirable for both removal and transferal. The PVA system is desirable due to its flexibility, rigidity, and solubility in water, while the Saran is very thin, flexible, and can be removed from the coated mandrel by exposing to temperatures $< -40°C$. The PVC and PBS systems are both brittle and shrink excessively when exposed to low temperatures.

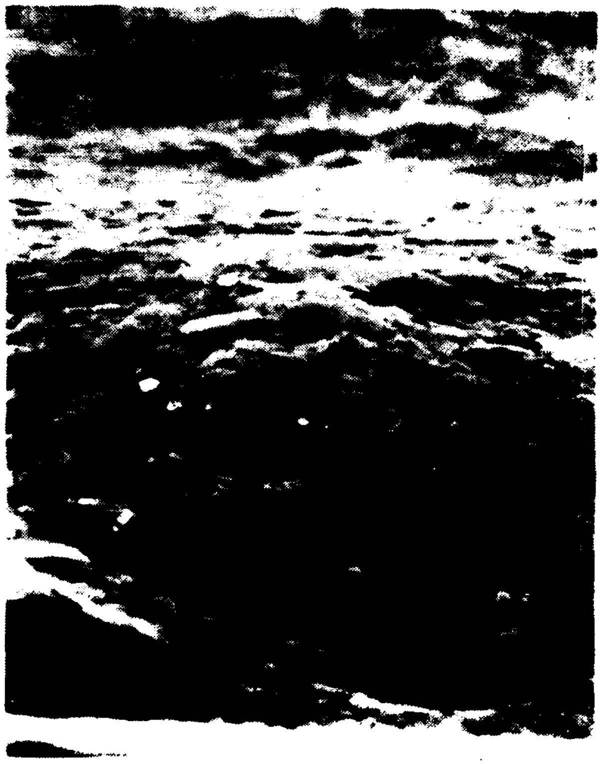


Figure 2. SEM PHOTOMICROGRAPH OF PYROLYTIC CARBON FILM EXHIBITING FLAT PLATELET (LAMINAR) STRUCTURE (BRITTLE FILM).

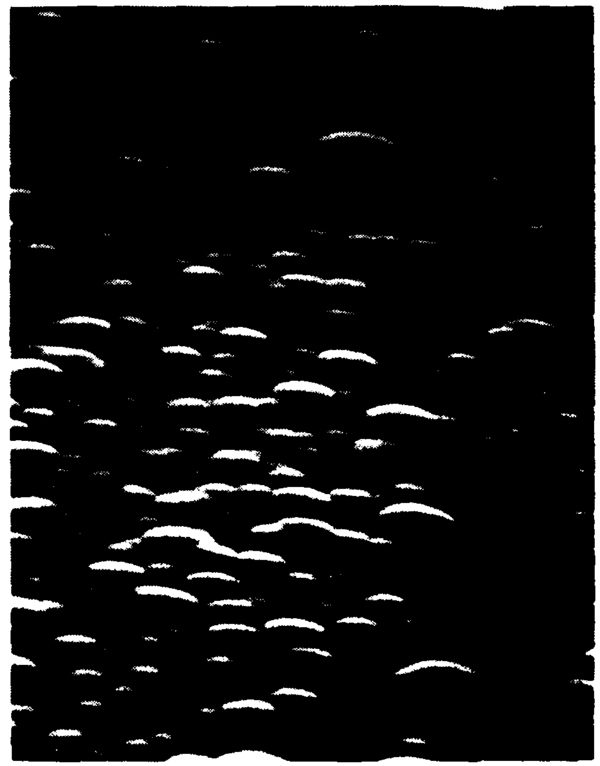


Figure 3. SEM PHOTOMICROGRAPH OF PYROLYTIC CARBON FILM EXHIBITING TURBOSTRATIC STRUCTURE (FLEXIBLE FILM).

Figure 4. Ten-cm-diameter Seamless Cylindrical Carbon Films Coated with Polyvinylidene Chloride (Saran). Total Thickness < 5 µm, Carbon Thickness < 1 µm.

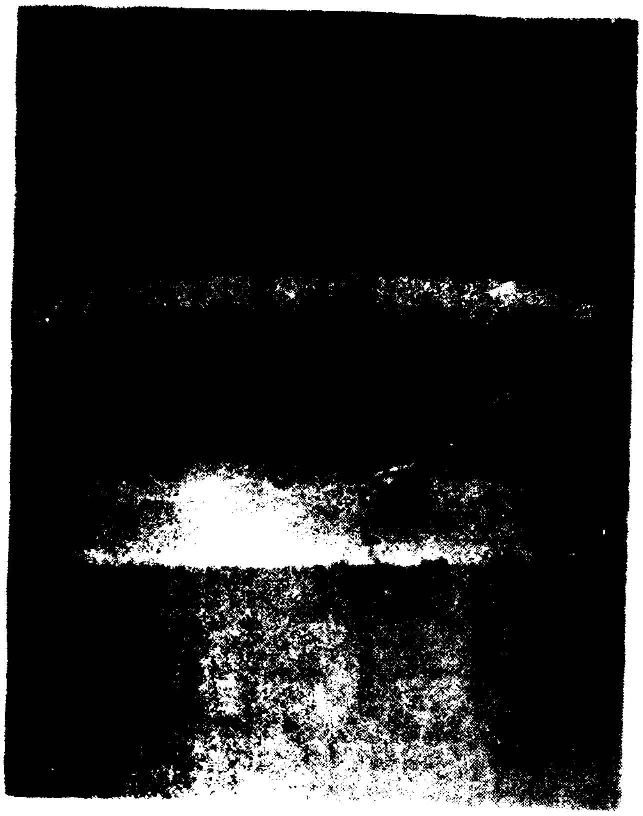


Figure 5. CARBON FILM REMOVED WITH BEESWAX.

Table 2

POLYMERIC COATINGS USED IN REMOVING PYROLYTIC CARBON FILM

Type of Polymeric Coating	Method	Results
PVA	Cutting	Good flexible film
PVA	Exposed to -40°C	
PVC	Exposed to -40°C	Excessive shrinkage, cracked film. Coated film becomes brittle after a few days
PBS	Exposed to -40°C	Excessive shrinkage, cracked film. Coated film becomes brittle after a few days
PBS	Cutting	Coated film not very flexible
Saran	Cutting	Did not release from quartz mandrel
Saran	-40°C	Excellent results, very thin and flexible film.

Naphthalene. The use of naphthalene in removing the carbon film from the quartz mandrel was chosen for evaluation because of its high vapor pressure, which makes it easy to eliminate once the separation is completed. However, several attempts at removing the carbon film from the mandrel with naphthalene proved unsuccessful because of the lack of adherence between the naphthalene and carbon film.

Expansion Disks. The use of expansion disks for film removal was also evaluated. This technique would eliminate the intermediate transferring agent such as wax and/or polymeric films. The expansion disk assembly, which is shown in Figure 6, consists of two 10-cm-diameter aluminum disks attached to a stainless steel tube passing through their center. The distance between the two disks, which is adjustable, was set at about 2 cm for this evaluation. The disk assembly is used by slipping the coated mandrel over the disks, which have been coated with either a contact cement or silicone adhesive. The coated mandrel is then held in place while applying heat to the aluminum disks which expand and come in contact with the carbon film. Upon cooling, the disks contract to their original size thus removing the carbon film from the fused silica mandrel. This method of film removal has not yet been completely successful due to incomplete release of the carbon film from the fused silica mandrel.

Other film removal and transferring methods to be investigated include: the use of cadmium and paralyene. Methods of separating or removing the polymeric coating from the carbon film will also be studied.

CONCLUSION

Fabrication of thin pyrolytic carbon seamless cylindrical films by CVD techniques has been successfully and reproducibly demonstrated. However, methods of removing and transferring these ultrathin films will require further development.

Several methods of film removal and transferring have been investigated, with the polymeric film removal technique exhibiting the best results. The fabrication process which consists of CVD coating a fused silica mandrel, removing the carbon film with a polymeric coating and mounting this coated film onto electrodes, is illustrated in Figure 7.

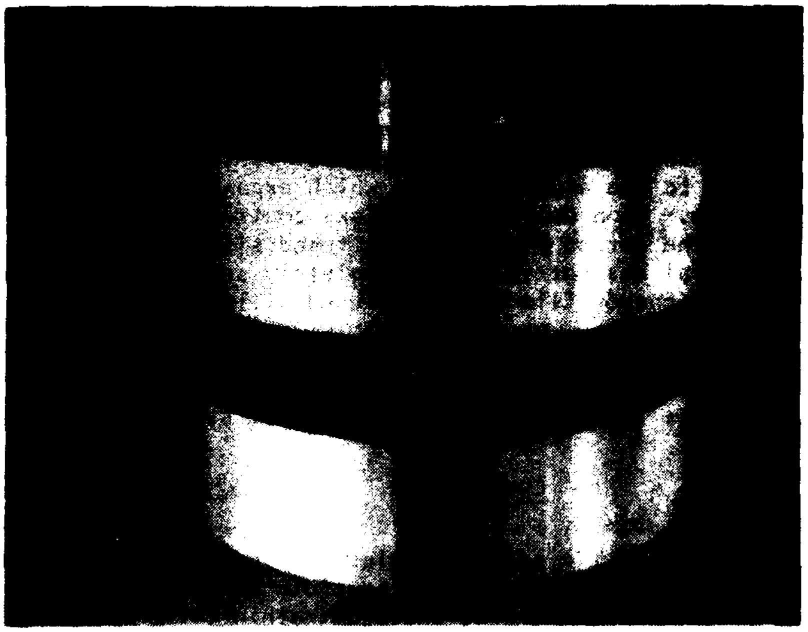
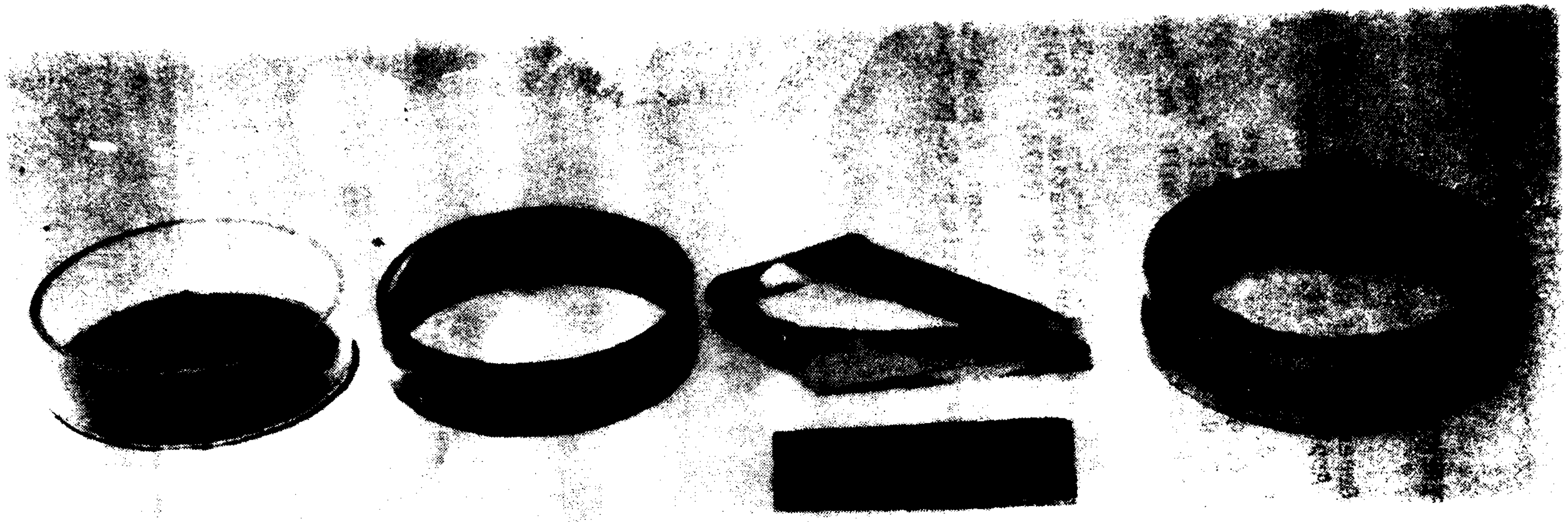


Figure 6. ALUMINUM EXPANSION DISKS USED IN REMOVING THIN CYLINDRICAL CARBON FILMS.



Fused Silica Mandrel — Carbon-Coated Mandrel Dipped in PVA — Carbon Film Coated with PVA — Coated Carbon Film Mounted on Electrodes

Figure 7. FABRICATION, REMOVAL, AND ATTACHMENT OF ULTRATHIN PYROLYTIC CARBON FILM.

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